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Lattice Parameter of Polycrystalline Diamond in the Low-Temperature Range

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The lattice parameter for polycrystalline diamond is determined as a function of temperature in the 4–300 K temperature range. In the range studied, the lattice parameter, expressed in angstrom units, of the studied sample increases according to the equation $a = 3.566810(12) + 6.37(41) \times 10^{-14}T^4$ (approximately, from 3.5668 to 3.5673 Å). This increase is larger than that earlier reported for pure single crystals. The observed dependence and the resulting thermal expansion coefficient are discussed on the basis of literature data reported for diamond single crystals and polycrystals.

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1. Introduction

Diamond is a key material in technology. Its applications are numerous; many of them are connected with mechanical (the highest hardness and bulk modulus known) and thermal (high thermal conductivity at room temperature (RT) and above) properties. Those related to diffraction and spectroscopy include its use:

- As a standard in diffraction experiments as proposed by Trzebiatowski in 1937 in an article entitled "Precise determination of lattice parameters of diamond and graphite" [1], and realised e.g. in its application in calibrating neutron-diffraction data for structure analysis [2]; wavelength calibration (polycrystalline internal standard) when using a synchrotron beam [3],
- as an optical element with synchrotron beams (single crystals) in monochromators or beam splitters, for synchrotron-beam position monitoring [4],
- for anvils (single crystals or sintered ceramics) in high pressure X-ray diffraction or optical/X-ray spectroscopy experiments.

Polycrystalline diamond is also reported to be applicable in electrocatalysis [5] and to be suitable for neutron filters [6], heatspreaders [7], for construction of surface acoustic wave devices [8], for radiation dosimetry [9], or for electrochemical detection of trace substances [10].

Owing to strong covalent bonding, diamond exhibits very low thermal expansion at low temperatures. Below room temperature, the total variation of the unit-cell dimension is less than 10^{-3} Å (below 50 K there is no variation at all), being comparable to the accuracy of lattice-parameter determination at a typical laboratory instrument. The only related materials where the variation is of such order of magnitude, is cubic boron nitride (borazon), and the rare hexagonal diamond (lonsdaleite) and boron nitride polymorphs. For other semiconductors the magnitude of variation is much larger, moreover, for some of them (Si, Ge) negative thermal expansion is observed at the lowest temperatures. Due to the extremely low expansivity, precise measurement of diamond lattice parameter as a function of temperature, and determination of the resulting thermal expansion coefficient (TEC), is a challenge.

The stability of the required wavelength is, at synchrotron beamlines, achieved using monochromators which have to work at thermomechanically fixed conditions. The stabilization problem (addressed e.g. in Refs. [3, 11–13]) is much reduced at modern beamlines. One of

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conditions of success is the use of cryocooled monochromator crystals. However, the wavelength fluctuations can still be visible for results of specific kinds of studies such as those employing the highest-resolution diffraction.

The instabilities would give an additional term to the lattice-parameter uncertainty, being hardly distinguishable for materials exhibiting thermal expansion of the order of 10 MK^{-1} or higher, but for some materials such as diamond where its magnitude is much smaller, the measurement conditions have to be carefully selected. Otherwise, the effect of fluctuation dominates over the physics of the thermal expansion.

Moreover, even for a single run some difficulties can be encountered in the Rietveld refinement process if the wavelength instabilities exceed some specific level. Therefore, at a synchrotron beamline the stability requirement is of similar importance as the generator stability and fixed temperature/humidity requirements at classical laboratories.

The data for the lattice parameter of diamond have been compiled and used to derive the thermal expansion coefficient in Ref. [14]. Detailed experimental investigations of $a(T)$ in the low temperature (LT) range have been performed using the Bond method for diamond single crystals [15, 16]. In Ref. [16], some influence of doping on thermal expansion has been found. Recently, similar observations (an increase of the $a(T)$ slope) have been made also for polycrystalline diamond (in 90–300 K range, only) [17]; moreover, boron doping causes a reduction of the lattice parameter value. Giles et al. [18] have derived the thermal expansion coefficient from X-ray forward diffraction using the synchrotron radiation. However, the $a(T)$ dependence has not been included in the cited study. In a most recent study a deviation of thermal expansion coefficient from the expected Debye law (T^3) has been reported [19]. One of difficulties in thin diamond film technology is the stress connected with the difference of TEC with respect to the substrate. A recent study shows that this problem can be reduced for the films of thickness in the nanometer range, as for them the expansion coefficient is larger [20].

Polycrystalline diamond is, as noted above, a material of interest for various applications. Its physical properties may somehow differ from those of single crystals, due, in particular, to a different defect density. To our knowledge, no detailed experimental study of lattice parameter for polycrystalline diamond concerns temperatures below 100 K.

In this work, the lattice parameter of polycrystalline diamond is experimentally determined as a function of temperature. The obtained lattice-parameter and thermal-expansion temperature dependence will be discussed on the basis of the available literature data.

2. Experiment

The measurements were performed with a commercial sample (Sigma-Aldrich #48,359-1 synthetic powder, of ≈ 1 μm monocrystalline grain size and purity of 99.9%), using the Debye–Scherrer geometry at beamline ID31 (ESRF) equipped with a Janis cryostat, providing temperature stability and accuracy better than ± 0.1 K over the entire temperature range.

The detection system was based on a bank of nine detectors preceded by Si(111) analyser crystals. The Debye–Scherrer method combined with a short wavelength is a proper one as one can minimize the systematic errors to a required level. Before the measurement session, wavelength was determined to be 0.394675 Å using NIST SRM640c standard Si. The whole measurement was conducted between storage-ring injections to avoid any abrupt wavelength changes. Similarly to Ref. [18], where the challenging thermal expansion of diamond has been reported, the monochromator was thermomechanically stable ensuring that the wavelength fluctuations are of the order of 2×10^{-5} Å, as verified by systematical measurements of the silicon standard.

Lattice parameters were calculated using the Rietveld refinement, via the Fullprof program [21]. 15 parameters were fitted: scale, overall B, lattice parameter, 3 width and 2 shape parameters and 7 background polynomial parameters. The pseudo-Voigt profile function was adopted.

3. Results

The refinement of the lattice parameters using the experimental powder diffraction patterns (for example cf. Fig. 1) yielded the values listed in Table I. The uncertainty at each temperature point is 5×10^{-6} Å (original *esd*'s multiplied by the sigma correction factor, SCOR = 1.6).

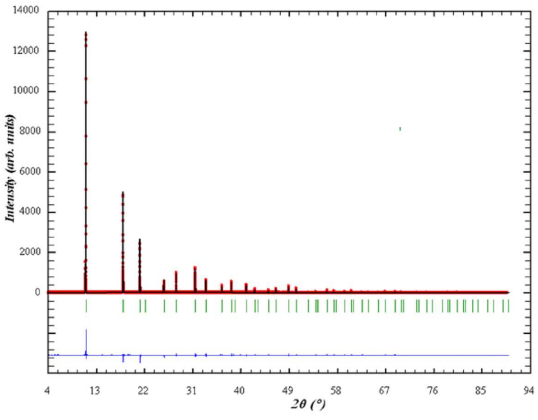

Fig. 1. Example of Rietveld refinement for diamond powder at $T = 25$ K.

Below room temperature, the total variation of the unit-cell dimension of diamond is about 0.5×10^{-4} Å, being comparable to the accuracy of lattice-parameter determination using a classical instrument, or even in routine studies employing synchrotron beams [17]. The

TABLE I

Lattice parameter of polycrystalline diamond as a function of temperature.

T [K]	a [Å]
4	3.566858(5)
25	3.566808(5)
50	3.566771(5)
80	3.566798(5)
110	3.566802(5)
140	3.566814(5)
170	3.566853(5)
200	3.566964(5)
230	3.566990(5)
260	3.567132(5)
295	3.567265(5)

obtained experimental lattice parameter dependence on temperature shows a difference in respect of single crystal data. Moreover, the absolute value of lattice parameter is larger for the present data, suggesting that for powder there may be a joint effect of impurities and defects resulting in impurity-induced lattice expansion and an increase of the thermal expansion coefficient. The *esd*'s provided by the Rietveld fitting are small. The fact that the scatter is larger (up to $\approx 5 \times 10^{-5}$ Å) is attributed to the effect of wavelength fluctuations. For comparison, in Ref. [12] describing a powder diffraction beamline, the wavelength drift of the magnitude as large as 1.6×10^{-5} Å as mentioned in section E therein, was attributed to the expansion of the support. The present result shows that at least in between the injections, at beamline ID31 the fluctuations have a magnitude small enough to study the challenging problem of diamond thermal expansion in the low temperature region.

TABLE II

Room-temperature thermal expansion coefficient for diamond. Abbreviations: XRD — X-ray diffractometry, XRBD — X-ray back diffractometry, DMA — dynamical mechanical analysis.

Material	Method	T [K]	Thermal expansion coeff. [MK^{-1}] at room temperature	Ref.	Year
experimental (powder)					
diamond dust	XRD	300	1.71	[1]	**1937**
powdered single crystal	XRD	300	1.38(12)	[23]	1951
boron doped diamond polycrystals	XRD	300	0.6–2.1	[17]	2006
diamond powder	**XRD**	**300**	**1.9**	this work	**2010**
experimental (other)					
diamond single crystal	dilatometry	273–323	1.18	[22]	1868
diamond	(XRD)	300	$\approx 1.03^a$	[24]	1977
diamond single crystal	XRD	300	1.25	[24]	1977
single crystal	XRD	300	1.0	[25]	1992
diamond	(XRD)	300	1.069^a	[14]	1996
diamond polycrystalline film, 0.3 mm thick	DMA, dilatometry	RT	0.7(±0.3)	[26]	1997
diamond single crystal (pure and doped)	XRD	300	1.0–1.6	[16]	2002
diamond single crystal	XRBD	(300)	(1.4)	[18]	2005
nanodiamond film	XRD	300	≈ 3.5	[20]	2009
calculated					
diamond		300	≈ 0.6	[27]	1991
diamond		300	≈ 1.0	[28]	2000
diamond		300	1.12	[29]	2006

[a] a value recommended by the cited authors

The $a(T)$ variation was satisfactorily fitted by the following polynomial:

$$a = 3.566810(12) + 6.37(41) \times 10^{-14} T^4 \,. \qquad (1)$$

In Fig. 2, this dependence is compared to that for an undoped single crystal [16].

The thermal expansion coefficient resulting from Eq. (1) is illustrated in Fig. 3. The resulting thermal expansion coefficient at 300 K is 1.9 MK^{-1} whereas the Debye-model fit provides a value compatible with earlier studies, 1.3 MK^{-1}. The discrepancy between these fits observed above 250 K is attributed to the fact that a simple polynomial approximation works the best at the lowest temperatures. Various values have been published for diamond TEC at room temperature. The scatter is

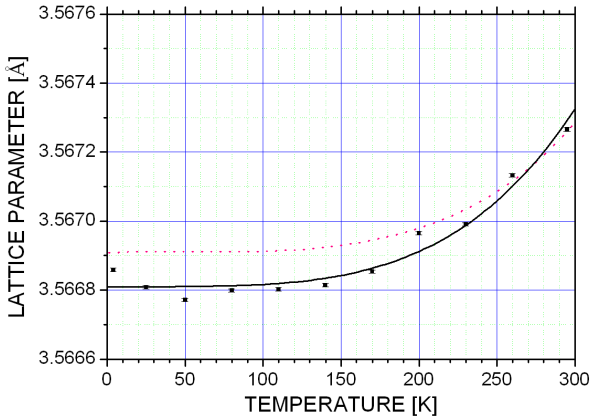

Fig. 2. Lattice parameter for polycrystalline diamond in the low-temperature range. The absolute values are based on calibration, at 300 K, to the SRM silicon standard. The *esd*'s are comparable to the symbol size. The dotted curve represents the data for pure (undoped) diamond single crystal [16]. For easier comparison with the present (calibrated) data, the single-crystal data are shifted from the original values by adding 9×10^{-4} Å.

quite large (cf. Table II where experimental [1, 14, 16, 18, 17, 20, 22–26] and theoretical [27–29] data are collected), illustrating the experimental and computational difficulties for this material. However, if the results for diamond powders (including the present result) and single crystals are distinguished, one easily observes that the TEC value at 300 K is by up to 30% higher for powders.

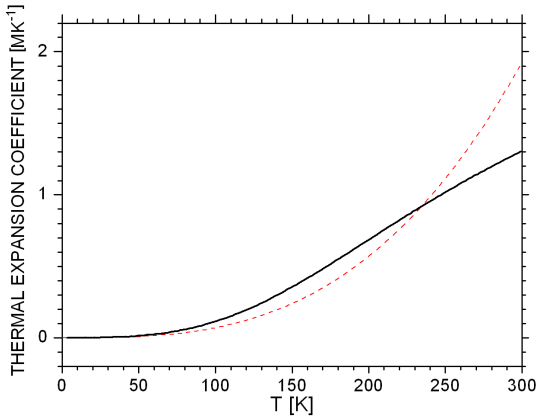

Fig. 3. Linear thermal expansion coefficient for polycrystalline diamond in the low-temperature range derived from the present data using two models for $a(T)$: Debye model (solid line), $A + Bx^4$ polynomial (dashed line).

The agreement with the 140-years-old result of Fizeau is worth noting. It illustrates the power of the old dilatometric method for TEC studies, unfortunately being limited, for anisotropic solids, to suitable single crystal samples.

4. Summary

In the present study, the temperature dependence of lattice parameter for commercial polycrystalline diamond is investigated. Variation of lattice parameter is determined for diamond polycrystal using high-resolution powder diffraction at a synchrotron beamline (ID31, ESRF). The variation is found to be by about 30% more pronounced as compared to previously reported data for pure diamond single crystal. The resulting thermal expansion coefficient values for diamond powders and polycrystals are briefly discussed and shown to be consistent with previously reported data. Of interest would be studies of thermal expansion of polycrystalline diamond as a function of the impurity level and crystallite size.

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